Magnetism and Superconductivity in Ruthenocuprates and Ruthenates. New Pathways to Novel Materials.

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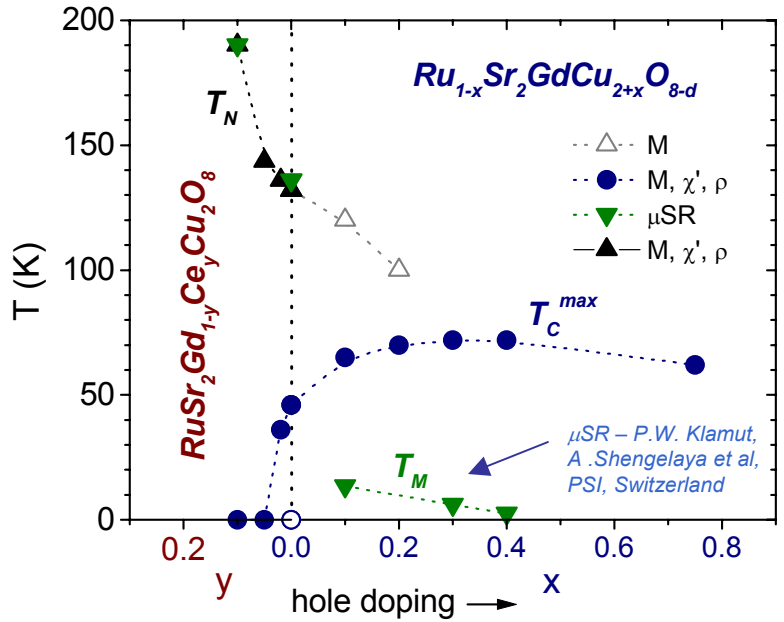
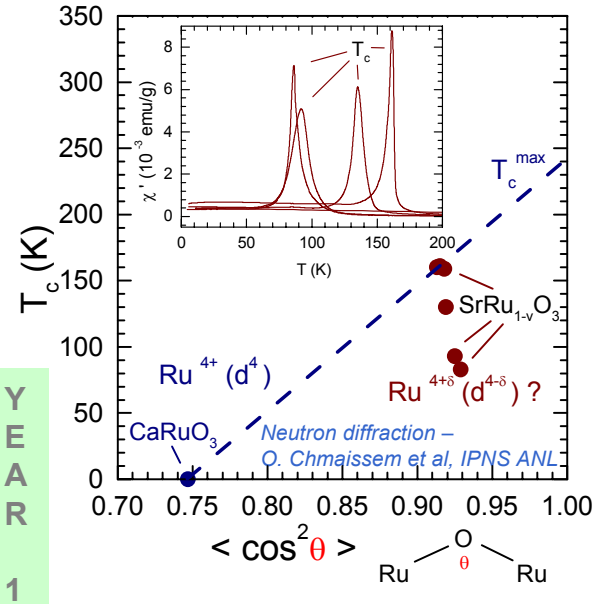
DMR-0105398

New family of magnetic superconductors by substitutions in layered $RuSr_2RECu_2O_8$

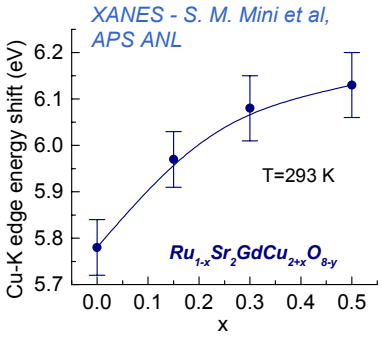
Discovery of cation nonstoichiometry effects in the metallic ferromagnet $SrRuO_3$



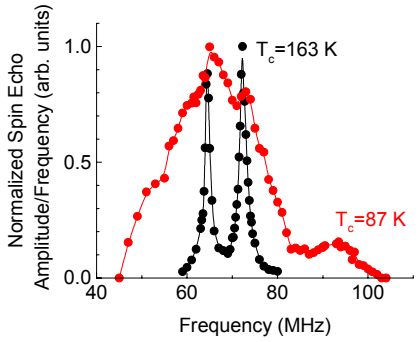


YEAR 1

Synthesis at elevated oxygen pressure produces non-stoichiometric $SrRu_{1-v}O_3$ perovskites with randomly distributed vacancies on the Ru-sites. The increased number of Ru vacancies rapidly suppresses the ferromagnetic T_c. Decrease of T_c can be associated with an increased formal valence of Ru and induced structural disorder.

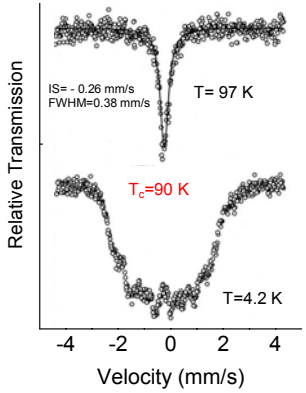


Investigation of substituted 1212-type ruthenocuprates led to the finding of novel low temperature magnetic transitions (T_M). Magnetic properties of the series of hole doped compositions suggest constrained dimensionality of the superconducting phase. Analogous Cu-doped 1222-type phases have been recently discovered and are currently being investigated in collaboration with I. Felner of Hebrew University, Israel



NMR - J. Budnick, W. Hines et al, University of Connecticut

Ru 99 Mössbauer - M. DeMarco et al, SUNY, Buffalo



Note for PPT slide on DMR-0105398

1212-type Ruthenocuprates

Recent reports of the apparent coexistence of superconductivity (SC) and ferromagnetism (FM) in ruthenocuprates have triggered intense interest in the properties of these materials. The compounds that exhibit this unusual behavior are $RuSr_2RECu_2O_8$ (Ru-1212) and $RuSr_2(RE_{2-x}Ce_x)Cu_2O_{10-y}$ (Ru-1222) (RE=Gd, Eu) and they belong to the family of high temperature superconductors (HTSC). Structurally similar to the well-known $GdBa_2Cu_3O_7$ (Gd123) superconductor, the ruthenocuprate $RuSr_2GdCu_2O_8$ is a layered perovskite containing both CuO_2 and RuO_2 planes in its crystal structure. In $RuSr_2GdCu_2O_8$, the magnetically ordered state manifests itself at temperatures T_N=130-136 K, much higher than the superconducting transition reported at 45 K for the highest T_C samples. The magnetic order persists in the superconducting state. What makes these compounds unique in the family of HTSC is that the magnetic ordering originates in the sublattice of the d-electron Ru ions. Recent muon spin rotation and magnetization results provided evidence for the coexistence of the magnetic ordering of Ru moments with superconductivity at low temperatures. Although the ferromagnetic ordering was initially proposed for the Ru sublattice below T_N, recent neutron diffraction experiments show that the dominant magnetic interactions are of the G-type antiferromagnetic (AFM) structure. Based on these results, the observed ferromagnetism should originate from the canting of the AFM lattice.

We report heterovalent substitutions in $RuSr_2RECu_2O_8$ that expand the range of magnetic and superconducting properties of this parent Ru-1212 ruthenocuprate to two new series of compounds: the hole doped $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-d}$ and the electron doped $RuSr_2Gd_{1-y}Ce_yCu_2O_8$. Study of these materials allow us to investigate the phase diagram (**Figure:** Tc –superconducting transition, T_N – Neel temperature for Ru sublattice ordering, T_M – likely the response of Cu sublattice vs. x, y) that links their properties to different hole doping achieved along the series. The magnetic properties of the series of $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ superconductors (maximum T_C = 72 K for x = 0.4) are indicative of the constrained dimensionality of the superconducting phase that apparently evolve along the series toward the quasi-two dimensional behavior characteristic for the x = 0 $RuSr_2GdCu_2O_8$ parent compound. Novel low temperature magnetic transitions for compositions x = 0.1, 0.3, 0.4 have been found from zero-field muon spin rotation experiments performed at Paul Scherrer Institute in Villigen, Switzerland.

Figure: X-ray Absorption Near Edge Spectroscopy (XANES) Cu-K edge energy shift vs. Cu→Ru substitution (x) in $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-d}$ series. The increase of an effective hole doping along the series (also seen in the Hall effect and Seebeck coefficient results) causes an increase of measured Cu-K edge energy. Experiments performed at Advanced Phonon Source, Argonne National Laboratory.

$SrRuO_3$

The relation of physical and structural properties to cation and oxygen non-stoichiometry in transition-metal perovskites has been a subject of intense research for several decades. Complex effects of non-stoichiometry were studied most extensively for 3d transition metals that acquire less extended electronic orbitals than the corresponding 4d ions. The 4d ruthenate $SrRuO_3$ with the perovskite crystal structure is known as a highly correlated, narrow-band metallic ferromagnet with a robust T_C=162 K. This compound has been intensively studied for possible application as an electrode material in microelectronic circuits. The results of substitution studies showed that the important factor controlling T_C is a change of the formal valence of Ru. For substitutions retaining the formal Ru^{4+} formal valence, the T_C decreases as a function of the decreasing Ru - O - Ru bond angle (similar to the T_N dependence observed for the single valent 3d transition metal perovskites of Fe, Mn, Cr, and Ni).

We report here on the decrease of T_C in nonstoichiometric $SrRu_{1-v}O_3$ perovskites synthesized for the first time at high-pressure oxygen conditions, which are expected to favor formation of the Ru^{5+} ions. Detailed neutron powder diffraction measurements indicate a random distribution of vacancies on the Ru crystallographic site, similar to the $LaMn_{1-v}O_3$ perovskites. Local-probe measurements (NMR, ^{99}Ru Mössbauer, EELS, XAFS) reveal the induced structural disorder that should also affect T_C through displacements of oxygen ions around Ru- and Sr- sites.

Figures:

T_c vs. $\langle\cos^2\theta\rangle$ for $CaRuO_3$ and $SrRuO_3$ synthesized in argon or air and for $SrRu_{1-v}O_3$ synthesized at 600 atm O_2. Based on the neutron diffraction data. Dashed line shows the relation: $T_c = T_m^{max} - C(1 - \langle\cos^2\theta\rangle)$, which relates T_c to departure from 180° of the B-O-B interaction angle (θ is the B-O-B bond angle) first introduced based on the model of super-exchange interaction for constant oxidation state antiferromagnetic orthoferrites $REFe^{3+}O_3$. Inset shows dependencies of the *ac* susceptibility (200Hz, 1 Oe) vs. temperature for $SrRu_{1-v}O_3$ samples with various T_c's.

Frequency dependence of ^{99,101}Ru zero-field spin-echo NMR spectra for two $SrRu_{1-v}O_3$ samples (T_c=160 K vs. 87 K). NMR spectrum for T_c=162 K sample (black line) consist of two well defined peaks at 64.4 MHz and 72.2 MHz corresponding to the ^{99}Ru and ^{101}Ru isotopes, respectively, and a hyperfine field of 329 kG. For sample with T_c=87 K (red curve), spectrum still shows the same two peaks at 64.4 MHz and 72.2 MHz. However, considerable broadening, along with an additional structure at both low and high frequency sides is observed and believed to be quadrupolar in origin. Peak frequencies and corresponding hyperfine field value of 329 kG are still consistent with the Ru^{4+} or low–spin (S=1) valence state.

^{99}Ru Mössbauer spectra at 97K and 4.2 K for $SrRu_{1-v}O_3$ sample with T_c=90 K. High temperature spectrum shows single broadened line. Combined with the low temperature spectrum, the results are suggestive of presence of electric quadruple interactions. Major component to the hyperfine magnetic field is about 330 kG. No significant difference in the isomer shift for T_c=162 K and T_c=90 K samples (-0.32 mm/sec vs. -0.26 mm/sec) is observed.